

# Foreword

It has been increasingly recognized that one of the major problems facing our generation and later ones is the reliance on fossil fuels, their effect on climate, their gradual exhaustion, and the great need for alternative energy sources. Since the most conspicuous and abundant source of energy is the sun, solar energy conversion has become the magical concept to conjure the development of organic and inorganic photovoltaics and, even better, the direct production of chemical energy carriers.

The focus of the present volume is on the many facets of new energy technologies where functional components reflect single features of the photosynthetic apparatus in nature. These features relate to the structure of the photosynthetic apparatus, its reaction kinetics and mechanisms, its underlying design and realization of analogs that mimic, in particular, photosystem II and its catalytic unit that is responsible for the splitting of water into oxygen and (bound) hydrogen. Related to the connected uptake and release of molecular hydrogen a number of chapters are also devoted to hydrogenase enzymes and mimics thereof.

The organization of the individual contributions into sections for *light harvesting*, *photochemical conversion* and *energy storage* in chemical bonds underlines both the complexity of natural photosynthesis and the problems associated with the transferability of biological strategies to large-scale solar technology. This wide ranging state-of-the-art presentation with its many vignettes of past history is also of interest to science history buffs. The present understanding of almost all fundamental aspects of photosynthesis rests on detailed knowledge of structure and organization of the photosynthetic apparatus as well as of its spectroscopic and kinetic fingerprints. The evolving features of Photosystem II over the past eighty years has seen, particularly in the last decade, a steady progress in atomic resolution of the crystal structure with foremost interest in the  $\text{Mn}_4\text{CaO}_5$  catalytic cluster, the role of its

environment and the many water molecules that may constitute the various ion and other delivery channels in the protein. In many cases synthetic analogs of this oxygen evolving apparatus are being sought, with and without electrodes, accompanied by structural studies and theoretical calculations and discussions of detailed mechanisms of the various reactions in these complex systems.

These studies of photosystems that generate energy-rich chemicals that can later be used to generate fuels inspire and complement a parallel approach involving photovoltaic cells where perhaps two may act in concert for water oxidation and hydrogen production, in the optimal version as tandem cells equipped with different light absorbers covering most of the solar spectrum. In many instances, theory plays a role in unifying the structural and spectroscopic information, assisting the understanding of the many chemical reactions, including the frequent transfer of electrons between different sites, proton and proton coupled-electron transfers, and various bond breaking bond forming reaction steps. Readers interested in pursuing or understanding the phenomena involved and assessing future perspectives reaching out to artificial enzymes, protein maquettes and synthetic biology will find in this book sound information on the basics of photosynthesis relevant for the production of solar fuels.

Rudolph A. Marcus

*California Institute of Technology  
Pasadena CA*

Maria-Elisabeth Michel-Beyerle

*Technical University of Munich  
Nanyang Technological University of  
Singapore*